

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 February 2002 (28.02.2002)

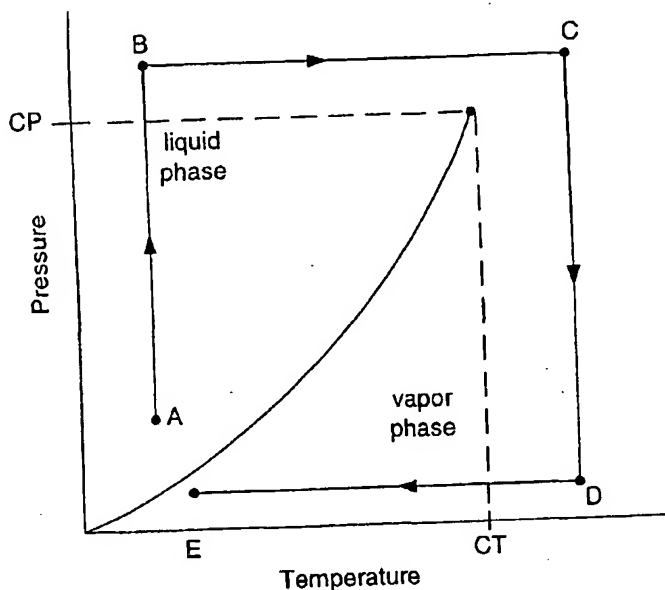
PCT

(10) International Publication Number
WO 02/17373 A1

- (51) International Patent Classification⁷: **H01L 21/316**, 21/768
- (74) Agent: **RODDY, Richard, J.**; Advanced Micro Devices, Inc., One AMD Place, Mail Stop 68, Sunnyvale, CA 94088-3453 (US).
- (21) International Application Number: **PCT/US01/18226**
- (22) International Filing Date: **4 June 2001 (04.06.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data: **09/643,531** **22 August 2000 (22.08.2000)** **US**
- (71) Applicant: **ADVANCED MICRO DEVICES, INC.** [US/US]; One AMD Place, Mail Stop 68, P.O. Box 3453, Sunnyvale, CA 94088-3453 (US).
- (72) Inventors: **RANGARAJAN, Bharath**; 2295 Dolores Avenue, Santa Clara, CA 95050 (US). **SUBRAMANIAN, Ramkumar**; 4271 Norwalk Drive, #X-105, San Jose, CA 95129 (US). **SINGH, Bhanwar**; 17122 Heatherwood Way, Morgan Hill, CA 95037 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report

[Continued on next page]

(54) Title: **SUPER CRITICAL DRYING OF LOW K MATERIALS**



(57) Abstract: One aspect of the present invention relates to a method of forming a low k material layer on a semiconductor substrate, involving the steps of depositing a mixture containing a low k material and a casting solvent on the semiconductor substrate; optionally contacting the mixture with a transition solvent whereby the casting solvent is removed from the mixture to form a second mixture containing the low k material and the transition solvent; contacting the second mixture with a supercritical fluid whereby the transition solvent is removed from the second mixture; and permitting the supercritical fluid to evaporate thereby forming the low k material layer.

WO 02/17373 A1



- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SUPER CRITICAL DRYING OF LOW K MATERIALS

TECHNICAL FIELD

The present invention generally relates to processing a semiconductor substrate. In particular, the present invention relates to methods of forming a high quality low k material layer on a semiconductor substrate using a supercritical fluid.

BACKGROUND ART

High performance integrated circuit chips contain of millions of transistors that perform various functions including random access memory, central processing communications, and the like. Each of the transistors is interconnected with electrically conducting elements. In order to efficiently accomplish this on a single chip, a typical integrated circuit chip contains multiple layers of conducting elements. Since there are size constraints associated with placing millions of conducting elements on a chip having an area of only a few square centimeters, the connecting elements themselves are very small, and the distance that separates conducting elements is small as well. For example, a state-of-the-art integrated circuit produced today has a conductor width of 0.18 to 0.25 μm and conductor spacing of 0.18 to 0.25 μm .

Dielectric materials are widely used in the semiconductor industry to separate structures on an integrated circuit chip, such as separating metal interconnect layers from active devices. Dielectrics are also used to separate two adjacent metal interconnect layers to prevent shorting between the metal layers. With an increasing number of levels in integrated circuit chips, there is growing emphasis on the quality of so-called interlevel dielectrics. This is because multiple levels of metal interconnects are necessary in order to achieve higher packing densities and smaller chip sizes with increased circuit complexity.

The smaller geometries raise certain electrical performance problems that are not of concern in older generation integrated circuits. The reduced spacing results in increased electrical capacitance, which in turn causes capacitive interconnect delay that can slow down the operational speed of the circuit. Increased capacitance increases the amount of power that the integrated circuit requires to operate. Increased capacitance also causes cross-talk that can result in generating signal errors.

Since the dimensions of current integrated circuits are constrained, and since the trend is to continue decreasing geometries, it is necessary to reduce the capacitance in integrated circuit chips. Conventional semiconductor fabrication commonly uses high density or conventional silicon dioxide and/or spin-on glass as a dielectric.

One disadvantage associated with high density silicon dioxide and/or spin-on glass dielectrics is their relatively high permittivity or dielectric constant. Typically, high density silicon dioxide and/or spin-on glass have a relative (to permittivity of free space) dielectric constant of 3.9 or higher. High dielectric constant materials produce capacitive loads on the adjacent conductors which degrades performance of both high frequency and high density transistors.

Another disadvantage associated with high density silicon dioxide and/or spin-on glass dielectrics is that thicker dielectric layers are required to compensate for the high dielectric constant. Thicker layers result in larger geometry devices, increasing the overall size and cost of the integrated circuit chip while reducing

functionality. Additionally, thick dielectric layers increase planarization problems, making it difficult to form multi-layer metallizations on top of the dielectrics.

An important factor for judging the quality of a dielectric is dielectric strength. Dielectric strength is typically referred to as breakdown voltage or breakdown field strength. Breakdown field strength is a property with units of volts per unit length at which an insulative material does not insulate, breaks down and results in a short circuit. Calculating the required minimum breakdown field strength for an integrated circuit involves taking the operating voltage of the circuit and dividing it by the separation distance between adjacent conducting elements. For example, in a 0.25 μm technology integrated circuit that operates at a voltage of 3.3 volts, the minimum breakdown field strength required is 3.3 volts divided by 0.25 microns, which equals 13.2 V/ μm , or 0.132 MV/cm. Typical safety margins are several times this or a minimum of about 0.5 MV/cm. The breakdown field strength of air is less than 1 volt per micron. Another factor for judging the quality of a dielectric is leakage current. Leakage current is low level current flux through an insulator of field strength less than the breakdown field strength. A typical requirement for an integrated circuit is a leakage current density less than 2×10^{-8} amps/ cm^2 and an applied electric field strength of 0.05 MV/cm.

Generally speaking, therefore, it is desirable to provide a dielectric material layer with a high breakdown field strength and low leakage current. Low k material layers are attractive in this respect because they possess both high breakdown field strength and low leakage current. However, there are problems associated with forming low k material layers. For instance, heat causes deleterious structural damage to a low k material layer or film (structural collapse of the low k material). Temperatures as low as 350°C can cause such damage in certain low k material layers. This is a problem because semiconductor processing often involves high temperature steps. Consequently, various layers used in fabricating semiconductor devices must be able to withstand high temperatures.

Another problem associated with low k material layers involves solvent removal after application. Incomplete solvent removal leads to undesirable increases in the dielectric constant of the subsequently formed low k material layer. Increases in the dielectric constant consequently degrade the electrical properties and thus the reliability of the electronic devices made with such low k materials. Incomplete solvent removal also provides a failure mechanism for a device formed with the low k material layer, since the unremoved solvent may vaporize out of the layer and damage another layer or structure within the device. Incomplete solvent removal is therefore a significant concern.

Yet another problem associated with low k material layers involves solvent removal by evaporation from low k material layers, in that evaporation creates high surface tension forces that sometimes induces deleterious structural collapse of the low k material layer.

DISCLOSURE OF THE INVENTION

The present invention provides methods for making semiconductor structures with low k insulation materials using a supercritical fluid. The present invention also provides methods for forming high quality low k material layers in semiconductor structures by minimizing and/or eliminating residual solvents in the low k material layers. The high quality low k material layers leads to the formation of electronic devices having desirable electrical properties. The low k material layers made in accordance with the present invention have at

least one of high temperature stability, the absence of residual solvent, a desirable structural network, high breakdown field strength and low leakage current.

One aspect of the present invention relates to a method of forming a low k material layer on a semiconductor substrate, involving the steps of depositing a mixture containing a low k material and a casting solvent on the semiconductor substrate; optionally contacting the mixture with a transition solvent whereby the casting solvent is removed from the mixture to form a second mixture containing the low k material and the transition solvent; contacting the mixture or second mixture with a supercritical fluid whereby the casting solvent or the transition solvent is removed from the mixture or the second mixture; and permitting the supercritical fluid to evaporate thereby forming the low k material layer.

Another aspect the present invention relates to a method processing a low k material, involving the steps of depositing a mixture comprising the low k material and a casting solvent on a semiconductor substrate wherein the casting solvent comprises at least one of deionized water, a water based dispersion, a water-in-oil emulsion, an oil-in-water emulsion, benzenes, chlorobenzenes, anisole, cyclohexanone, a lower alkyl alcohol, a lower alkyl ketone, and a lower alkyl ester, wherein each alkyl group has 5 or less carbon atoms; contacting the mixture with a transition solvent whereby the casting solvent is removed from the mixture to form a second mixture comprising the low k material and the transition solvent, wherein the transition solvent comprises at least one of a lower alkyl alcohol, a lower alkyl ketone, and a lower alkyl ester, wherein each alkyl group has 5 or less carbon atoms; contacting the second mixture with a supercritical fluid whereby the transition solvent is removed from the second mixture; and permitting the supercritical fluid to evaporate thereby forming a low k material layer having a dielectric constant below about 3.8.

Yet another aspect of the present invention relates to a method of making a low k dielectric layer, involving the steps of depositing a mixture comprising a low k material and a casting solvent on a semiconductor substrate; contacting the mixture with an organic solvent whereby the casting solvent is removed from the mixture to form a second mixture comprising the low k material and the organic solvent, wherein the organic solvent comprises at least one of a ketone, an ester, an alcohol, an ether, and an aromatic hydrocarbon; contacting the second mixture with a supercritical fluid using spin coating whereby the organic solvent is removed from the second mixture, wherein the supercritical fluid comprises at least one of CO_2 , N_2O , C_2H_6 , CFH_3 , H_2O , NH_3 , and CClF_3 ; and permitting the supercritical fluid to evaporate thereby forming the low k dielectric layer having a dielectric constant below about 3.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows a method of forming a supercritical fluid in the context of a phase diagram according to one aspect of the present invention.

Figure 2 shows another method of forming a supercritical fluid in the context of a phase diagram according to another aspect of the present invention.

MODES FOR CARRYING OUT THE INVENTION

The present invention involves forming high quality, well defined low k material layers in semiconductor devices using a supercritical fluid. Generally speaking, this is accomplished by depositing a low

k material in a casting solvent onto a wafer, optionally contacting a transition solvent with the wafer, and then contacting a supercritical fluid with the wafer.

Low k materials are insulation materials; that is, a material with a low dielectric constant. Low k materials provide electrical insulation between various layers, devices, structures, and regions within semiconductor substrates. For purposes of this invention, low k materials have a dielectric constant below about 3.8. In another embodiment, low k materials have a dielectric constant below about 3. In yet another embodiment, low k materials have a dielectric constant below about 2.5. In still yet another embodiment, low k materials have a dielectric constant below about 2.0.

General examples of low k materials include low k polymers, low k fluorine containing compounds, and low k fluoropolymers. Examples of low k materials include polyimides, fluorinated polyimides, polysilsequioxane, benzocyclobutene (BCB), fluorinated benzocyclobutene, fluorosilicate glass, silicon oxyfluoride, fluorinated polysilicon, polyphenylquinoxaline, copolymers of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole, perfluoroalkoxy resin, fluorinated ethylene propylene, fluoromethacrylate, poly(arylene ether), parylene F, parylene N, amorphous polytetrafluoroethylene, and low density glass such as low density silicon dioxide. Low density silicon dioxide may be made using sol-gel techniques.

Specific examples of a commercially available low k materials include those under the trade designations FlareJ from AlliedSignal, believed to be derived from perfluorobiphenyl and aromatic bisphenols; Black DiamondJ from Applied Materials; ALCAP-S from Asahi Chemical; SiLK7 and Cyclotene7 BCB from Dow Chemical; Teflon7 polytetrafluoroethylene from DuPont; XLK and 3MS from Dow Corning; HSG RZ25 from Hitachi Chemical; HOSPJ and NanoglassJ from Honeywell Electronic Materials; LKD from JSR Microelectronics; CORALJ and AF4 from Novellus; mesoporous silica from Battelle PNNL; and VeloxJ PAE-2 from Schumacher.

The low k material is provided over a semiconductor substrate in a casting solvent. The semiconductor substrate is typically a silicon substrate optionally with various elements and/or layers thereover; including metal layers, barrier layers, dielectric layers, device structures, active elements and passive elements including polysilicon gates, wordlines, source regions, drain regions, bit lines, bases, emitters, collectors, conductive lines, conductive plugs, etc. The substrate may be static or spinning, and the low k materials in the casting solvent are applied by any suitable technique including spin-on techniques. If the low k material/casting solvent is provided over a static substrate, the substrate may be spun to remove excess solvent.

The casting solvent provides a vehicle to apply the low k material to a substrate surface. Casting solvents, as the term is used herein, are those solvents commonly employed to apply low k materials to semiconductor substrate surfaces. Examples of casting solvents include deionized water, suitable organic solvents, organic monomer mixtures, water based dispersions, water-in-oil emulsions, and oil-in-water emulsions (oil meaning organic solvent). Suitable organic solvents are organic compounds that do not dissolve out low k materials, such as benzenes, halobenzenes including chlorobenzenes, anisole, cyclohexanone, lower alkyl alcohols, lower alkyl ketones, and lower alkyl esters and the like. Examples of lower alkyl alcohol, lower alkyl ketone, and lower alkyl ester casting solvents are provided below in the discussion of transition solvents and thus are not repeated here. The casting solvent may alternatively or additionally include a water-soluble

monomer. Water soluble monomers generally comprise at least one of acrylamide, methacrylamide, acrylic acid, methacrylic acid, an acrylic acid salt, vinyl pyrrolidone, and vinyl acetate.

5 In embodiments where the casting solvent is compatible with the low k material and the subsequently employed supercritical fluid, it is not necessary to employ a transition solvent. The casting solvent is compatible with the subsequently employed supercritical fluid if the two substances are miscible. In embodiments where the casting solvent is not compatible with at least one of the low k material and the subsequently employed supercritical fluid, it is necessary to employ a transition solvent. It is in this connection that, after the low k material in a casting solvent is provided over a semiconductor substrate, a transition solvent is optionally applied to the substrate by any suitable technique.

10 The transition solvent is compatible with the low k material and the subsequently employed supercritical fluid. The transition solvent is compatible with the subsequently employed supercritical fluid if the two substances are miscible. The transition solvent displaces the casting solvent, as the casting solvent is removed from the low k material mixture. The casting solvent is removed in that it is at least substantially removed (although a small amount may remain) and preferably completely removed. In a preferred
15 embodiment, the transition solvent is at a temperature within about 10°C (higher or lower) of the temperature of the casting solvent. The transition solvent may be deposited on a static or spinning substrate containing the low k material. Typically, the transition solvent is deposited on a static substrate, optionally followed by agitation or spinning.

20 Transition solvents are typically organic solvents, but inorganic fluids such as water including deionized water may be employed. Preferred transition solvents are lower alkyl alcohols, lower alkyl ketones, and lower alkyl esters. Lower alkyl, for purposes of this invention, means alkyl groups having 5 or less carbon atoms (it is understood that certain compounds, such as ketones and esters, have two or more alkyl groups; and the 5 or less carbon atoms applies to each group). In this connection, methyl amyl ketone is a lower alkyl ketone.

25 Suitable transition solvents are inorganic or organic solvents including water, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, mesityl oxide, methyl amyl ketone, cyclohexanone and other aliphatic ketones; esters such as methyl acetate, ethyl acetate, iso-amyl acetate, alkyl carboxylic esters; ethers such as methyl t-butyl ether, dibutyl ether, methyl phenyl ether and other aliphatic or alkyl aromatic ethers; glycol ethers such as ethoxy ethanol, butoxy ethanol, ethoxy-2-propanol, propoxy ethanol, butoxy propanol and
30 other glycol ethers; glycol ether esters such as butoxy ethoxy acetate, ethyl 3-ethoxy propionate and other glycol ether esters; alcohols such as methanol, ethanol, propanol, iso-propanol, butanol, iso-butanol, amyl alcohol and other aliphatic alcohols; aromatic hydrocarbons such as benzene, toluene, xylene, and other aromatics or mixtures of aromatic solvents, naphthalene and mineral spirits, and nitro alkanes such as 2-nitropropane. Mixtures of two or more transition solvents may be employed. Preferred transition solvents include ethanol,
35 acetone, methyl ethyl ketone, methyl isobutyl ketone, amyl alcohol, iso-amyl alcohol, amyl acetate, and iso-amyl acetate.

In some embodiments where a transition solvent is employed, the casting solvent and the transition solvent are different compounds (or mixtures of compounds). In other embodiments where a transition solvent is employed, the casting solvent and the transition solvent are the same compounds (or same mixtures of

compounds). In these embodiments, it is sometimes desirable to provide clean or fresh solvent to displace contaminated or debris containing casting solvent.

After the casting solvent or the transition solvent is contacted with the low k material covered substrate surface, a supercritical fluid is applied to the substrate. The supercritical fluid displaces the casting solvent or the transition solvent, as the casting solvent and/or the transition solvent is substantially removed from the low k material mixture. A supercritical fluid is a fluid medium that is at a temperature that is sufficiently high that it cannot be liquified by pressure. A supercritical fluid relates to dense gas solutions with enhanced solvation powers, and can include near supercritical fluids. The basis for a supercritical fluid is that at a critical temperature and pressure, the liquid and gas phases of a single substance can co-exist.

The supercritical fluid phenomenon is documented, see pages F-62 to F-64 of the CRC Handbook of Chemistry and Physics, 67th Edition, 1986-1987, published by the CRC Press, Inc., Boca Raton, Fla.. At high pressures above the critical point, the resulting supercritical fluid, or "dense gas", attains densities approaching those of a liquid and assumes some of the properties of a liquid. These properties are dependent upon the fluid composition, temperature, and pressure. As used herein, the "critical point" is the transition point at which the liquid and gaseous states of a substance merge with each other and represents the combination of the critical temperature and critical pressure for a given substance.

The compressibility of supercritical fluids is great just above the critical temperature where small changes in pressure result in large changes in the density of the supercritical fluid. The "liquid-like" behavior of a supercritical fluid at higher pressures results in greatly enhanced solubilizing capabilities compared to those of the "subcritical" compound, with higher diffusion coefficients and an extended useful temperature range compared to liquids. An interesting phenomenon associated with supercritical fluids is that as the pressure increases, the solubility of the solute often increases by many orders of magnitude with only a small pressure increase.

Near-supercritical liquids also demonstrate solubility characteristics and other pertinent properties similar to those of supercritical fluids. Fluid "modifiers" can often alter supercritical fluid properties significantly, even in relatively low concentrations. In one embodiment, a fluid modifier is added to the supercritical fluid. These variations are considered to be within the concept of a supercritical fluid as used in the context of this invention. Therefore, as used herein, the phrase "supercritical fluid" also denotes a compound above, at, or slightly below the critical temperature and pressure (the critical point) of that compound.

Examples of compounds which are known to have utility as supercritical fluids are given in Table 1.

TABLE 1

5	Compound	EXAMPLES OF SUPERCRITICAL FLUIDS			
		Boiling Point (°C)	Critical Temperature (°C)	Critical Pressure (atm)	Critical Density (g/cm ³)
	CO ₂	-78.5	31.3	72.9	0.448
10	NH ₃	-33.35	132.4	112.5	0.235
	H ₂ O	100.00	374.15	218.3	0.315
	N ₂ O	-88.56	36.5	71.7	0.45
	Xenon	-108.3	16.6	57.6	0.118
	Krypton	-153.2	-63.8	54.3	0.091
15	Methane	-164.00	-82.1	45.8	0.2
	Ethane	-88.63	32.28	48.1	0.203
	Ethylene	-103.7	9.21	49.7	0.218
	Propane	-42.1	96.67	41.9	0.217
	Pentane	36.1	196.6	33.3	0.232
20	Methanol	64.7	240.5	78.9	0.272
	Ethanol	78.5	243.0	63.0	0.276
	Isopropanol	82.5	235.3	47.0	0.273
	Isobutanol	108.0	275.0	42.4	0.272
	CClF ₃	-31.2	28.0	38.7	0.579
25	CFH ₃	-78.4	44.6	58.0	0.3
	Cyclohexanol	155.65	356.0	38.0	0.273

Due to the low cost, environmental acceptability, non-flammability, and low critical temperature of carbon dioxide, nitrous oxide, and water, supercritical carbon dioxide, nitrous oxide and/or H₂O fluid is preferably employed in the present invention.

The supercritical fluid is applied to the substrate containing the low k material and the casting solvent or the transition solvent in any suitable manner. For example, the wafer containing the low k material and the casting solvent or the transition solvent is present in a high pressure chamber. The chamber is flooded with the compound that forms the supercritical fluid (such as carbon dioxide) in liquid form. The pressure is then increased above the critical pressure, followed by raising the temperature above the critical temperature, thereby converting the compound that forms the supercritical fluid into a supercritical fluid. Next, the pressure is decreased to ambient pressure and the temperature is lowered to room temperature.

This method of contacting the wafer containing the low k material and the casting solvent or the transition solvent with the supercritical fluid is graphically illustrated in Figure 1. Referring to Figure 1, a phase diagram is shown with the pressure on the y-axis and the temperature on the x-axis. The critical temperature is

represented by CT and the critical pressure is represented by CP. The line originating at the origin is the liquid-vapor interface. Point A refers to flooding the chamber with the compound that forms the supercritical fluid in liquid form. Increasing the pressure above the critical pressure is shown by the line from point A to point B; raising the temperature above the critical temperature is shown by the line from point B to point C; decreasing the pressure to ambient pressure is shown by the line from point C to point D; and decreasing the temperature to room temperature is shown by the line from point D to point E. Alternatively, any number of steps (a discrete pressure and temperature increase or decrease) may be employed, so long as the liquid-vapor interface line is not crossed.

Since the liquid-vapor interface line is not crossed when forming the supercritical fluid, interfacial tension forces associated with the liquid-vapor interface are avoided. Such interfacial tension forces may, in some instances, collapse the three dimensional network of the low k material.

Alternatively, after the wafer containing the low k material and the casting solvent or the transition solvent is provided in the high pressure chamber and the chamber is flooded with the compound that forms the supercritical fluid in liquid form, the pressure and temperature are raised simultaneously to the critical temperature and pressure ensuring that the liquid phase of the compound that forms the supercritical fluid remains in liquid form.

This method of contacting the wafer containing the low k material and the casting solvent or the transition solvent with the supercritical fluid is graphically illustrated in Figure 2. Referring to Figure 2, a phase diagram is shown with the pressure on the y-axis and the temperature on the x-axis, wherein the critical temperature is represented by CT and the critical pressure is represented by CP, and the line originating at the origin is the liquid-vapor interface. Point A refers to flooding the chamber with the compound that forms the supercritical fluid in liquid form. Simultaneously increasing the pressure and temperature above the critical pressure is shown by the line from point A to point C; decreasing the pressure is shown by the line from point C to point F; and simultaneously decreasing the temperature to room temperature and ambient pressure is shown by the line from point F to point E. Again, since the liquid-vapor interface line is not crossed when forming the supercritical fluid, interfacial tension forces associated with the liquid-vapor interface are avoided.

The supercritical fluid, after replacing the casting solvent or the transition solvent, Aevaporates@, out-gases or otherwise is removed from the low k material without causing any structural damage to the three dimensional network of the low k material. The supercritical fluid is removed completely or at least substantially completely. While not wishing to be bound by any theory, it is believed that this is because detrimental surface tension forces, which can damage the microstructure of the three dimensional network of the low k material, are avoided since there is no liquid-air interface associated with a supercritical fluid. Moreover, since the supercritical fluid is easily and completely removed from the low k material, residual solvent concerns are minimized and/or eliminated (or alternatively, there are inconsequential small residual amounts). Since residual solvent concerns are minimized, problems such as increases in the dielectric constant of the subsequently formed low k material layer and solvent outgassing induced damage to other layers within the device are minimized and/or eliminated.

The microstructure of the three dimensional network of the low k material formed in accordance with the present invention is characterized by numerous pores or air pockets (in other words, Aspongy®). The air pockets provide insulation characteristics to the low k material layer, as air has a dielectric constant of 1.

Optionally, after the supercritical fluid is contacted with the low k material covered substrate surface, the substrate may be heated or baked for a short period of time to ensure that the supercritical fluid is completely removed from the low k material.

The thickness of the low k material layer formed in accordance with the present invention is not critical to the invention. In one embodiment, however, the thickness of the resulting low k material layer is from about 200 Å to about 20,000 Å. In another embodiment, the thickness of the resulting low k material layer is from about 500 Å to about 10,000 Å. In yet another embodiment, the thickness of the resulting low k material layer is from about 1,000 Å to about 5,000 Å.

Low k material layers formed in accordance with the present invention have a lower dielectric constant and/or a higher breakdown voltage than low k material layers formed in conventional manners (in instances where the comparison involves the same low k material). In one embodiment, the low k material layers formed in accordance with the present invention have at least about a 5% lower dielectric constant and/or at least about a 5% higher breakdown voltage than low k material layers formed in conventional manners. In another embodiment, the low k material layers formed in accordance with the present invention have at least about a 10% lower dielectric constant and/or at least about a 10% higher breakdown voltage than low k material layers formed in conventional manners.

Although the invention has been shown and described with respect to a certain preferred embodiment or embodiments, it is obvious that equivalent alterations and modifications will occur to others skilled in the art upon the reading and understanding of this specification and the annexed drawings. In particular regard to the various functions performed by the above described components (assemblies, devices, circuits, etc.), the terms (including any reference to a Means®) used to describe such components are intended to correspond, unless otherwise indicated, to any component which performs the specified function of the described component (i.e., that is functionally equivalent), even though not structurally equivalent to the disclosed structure which performs the function in the herein illustrated exemplary embodiments of the invention. In addition, while a particular feature of the invention may have been disclosed with respect to only one of several embodiments, such feature may be combined with one or more other features of the other embodiments as may be desired and advantageous for any given or particular application.

INDUSTRIAL APPLICABILITY

The methods of the present invention are useful generally in the field of thin film formation and semiconductor processing and may be specifically employed in at least one of the fields of microprocessor fabrication and semiconductor memory device fabrication.

CLAIMS

What is claimed is:

1. A method of forming a low k material layer on a semiconductor substrate, comprising:
 - 5 depositing a mixture comprising a low k material and a casting solvent on the semiconductor substrate;
 - optionally contacting the mixture with a transition solvent whereby the casting solvent is removed from the mixture to form a second mixture comprising the low k material and the transition solvent,
 - 10 wherein the transition solvent comprises at least one of a lower alkyl alcohol, a lower alkyl ketone, and a lower alkyl ester, wherein each alkyl group has 5 or less carbon atoms;
 - contacting the mixture or the second mixture with a supercritical fluid whereby the casting solvent or the transition solvent is removed from the mixture or the second mixture; and
 - 15 permitting the supercritical fluid to evaporate thereby forming the low k material layer.
2. The method of claim 1, wherein the casting solvent comprises at least one of deionized water, a water based dispersion, a water-in-oil emulsion, an oil-in-water emulsion, benzenes, chlorobenzenes, anisole, cyclohexanone, acetone, methyl ethyl ketone, methyl isobutyl ketone, mesityl oxide, methyl amyl ketone, cyclohexanone, methyl acetate, ethyl acetate, iso-amyl acetate, alkyl carboxylic esters, methyl t-butyl ether, dibutyl ether, methyl phenyl ether, ethoxy ethanol, butoxy ethanol, ethoxy-2-propanol, propoxy ethanol, butoxy propanol, butoxy ethoxy acetate, ethyl 3-ethoxy propionate, methanol, ethanol, propanol, iso-propanol, butanol, iso-butanol, amyl alcohol, benzene, toluene, xylene, naphthalene, mineral spirits, and 2-nitropropane.
- 25 3. The method of claim 1, wherein the supercritical fluid comprises at least one of CO_2 , N_2O , H_2O , C_2H_6 , CFH_3 , CClF_3 , NH_3 , xenon, krypton, methane, ethylene, propane, pentane, methanol, ethanol, isopropanol, isobutanol, and cyclohexanol.
4. The method of claim 1, wherein the low k material comprises at least one of a polyimide, a fluorinated polyimide, a polysilsequioxane, benzocyclobutene, a fluorinated benzocyclobutene, a fluorosilicate glass, silicon oxyfluoride, fluorinated polysilicon, polyphenylquinoxaline, a copolymer of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole, a perfluoroalkoxy resin, fluorinated ethylene propylene, fluoromethacrylate, poly(arylene ether), parylene F, parylene N, amorphous polytetrafluoroethylene, and low density silicon dioxide.
- 35 5. The method of claim 1, wherein the supercritical fluid has a critical temperature and pressure and is formed by providing a composition in a liquid phase, raising the pressure of the composition above the critical pressure, and raising the temperature above the critical temperature.

6. The method of claim 1, further comprising, after depositing the mixture comprising the low k material and the casting solvent on the semiconductor substrate, contacting the mixture with a transition solvent whereby the casting solvent is removed from the mixture to form a second mixture comprising the low k material and the transition solvent; then contacting the second mixture with the supercritical fluid whereby the transition solvent is removed from the second mixture; and permitting the supercritical fluid to evaporate thereby forming the low k material layer,

wherein the transition solvent comprises at least one of acetone, methyl ethyl ketone, methyl isobutyl ketone, mesityl oxide, methyl amyl ketone, cyclohexanone, methyl acetate, ethyl acetate, iso-amyl acetate, alkyl carboxylic esters, methyl t-butyl ether, dibutyl ether, methyl phenyl ether, ethoxy ethanol, butoxy ethanol, ethoxy-2-propanol, propoxy ethanol, butoxy propanol, butoxy ethoxy acetate, ethyl 3-ethoxy propionate, methanol, ethanol, propanol, iso-propanol, butanol, iso-butanol, amyl alcohol, benzene, toluene, xylene, naphthalene, mineral spirits, and 2-nitropropane.

7. A method processing a low k material, comprising:

depositing a mixture comprising the low k material and a casting solvent on a semiconductor substrate wherein the casting solvent comprises at least one of deionized water, a water based dispersion, a water-in-oil emulsion, an oil-in-water emulsion, benzenes, chlorobenzenes, anisole, cyclohexanone, a lower alkyl alcohol, a lower alkyl ketone, and a lower alkyl ester, wherein each alkyl group has 5 or less carbon atoms;

contacting the mixture with a transition solvent whereby the casting solvent is removed from the mixture to form a second mixture comprising the low k material and the transition solvent, wherein the transition solvent comprises at least one of a lower alkyl alcohol, a lower alkyl ketone, and a lower alkyl ester, wherein each alkyl group has 5 or less carbon atoms;

contacting the second mixture with a supercritical fluid whereby the transition solvent is removed from the second mixture; and

permitting the supercritical fluid to evaporate thereby forming a low k material layer having a dielectric constant below about 3.8.

8. The method of claim 7, wherein the supercritical fluid has a critical temperature and pressure and is formed by providing a composition in a liquid phase, and simultaneously raising the pressure of the composition above the critical pressure and the temperature above the critical temperature.

9. A method of making a low k dielectric layer, comprising:

depositing a mixture comprising a low k material and a casting solvent on a semiconductor substrate;

contacting the mixture with an organic solvent whereby the casting solvent is removed from the mixture to form a second mixture comprising the low k material and the organic solvent, wherein the organic solvent comprises at least one of a ketone, an ester, an alcohol, an ether, and an aromatic hydrocarbon;

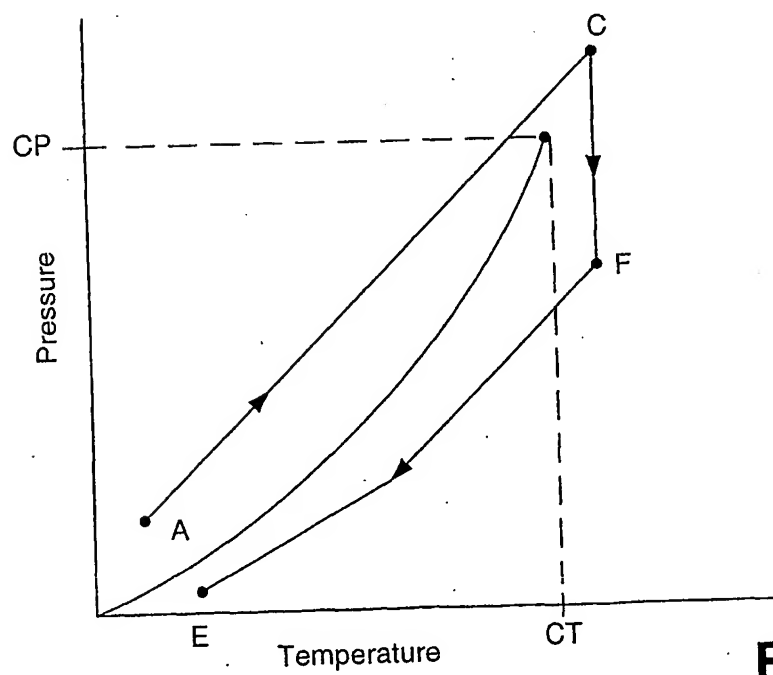
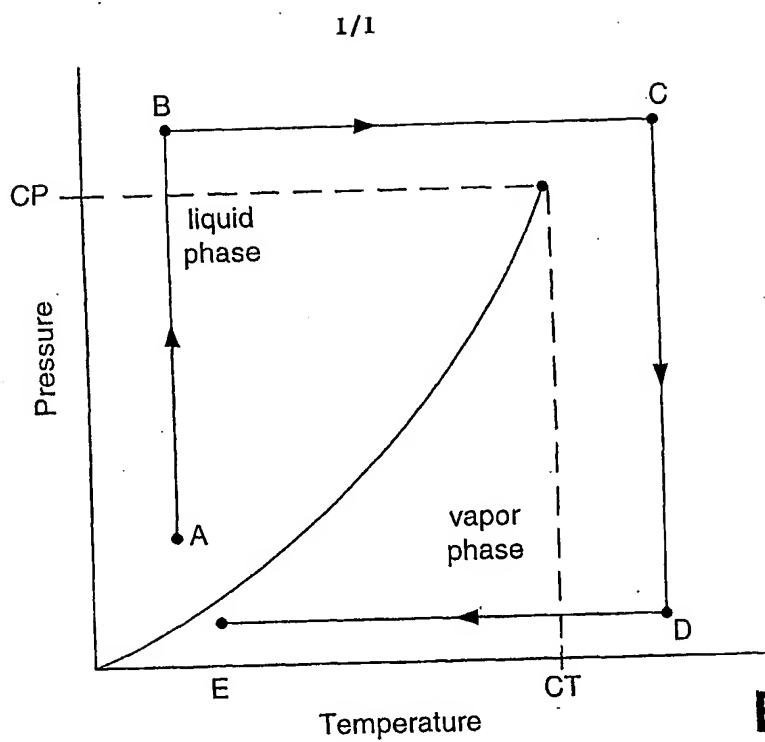
contacting the second mixture with a supercritical fluid using spin coating whereby the organic solvent is removed from the second mixture, wherein the supercritical fluid comprises at least one of CO₂, N₂O, C₂H₆, CFH₃, H₂O, NH₃, and CClF₃; and

5 permitting the supercritical fluid to evaporate thereby forming the low k dielectric layer having a dielectric constant below about 3.

10 10. The method of claim 9, wherein the low k material comprises at least one of a polyimide, a fluorinated polyimide, a polysilsequioxane, benzocyclobutene, a fluorinated benzocyclobutene, a fluorosilicate glass, silicon oxyfluoride, fluorinated polysilicon, polyphenylquinoxaline, a copolymer of 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole, a perfluoroalkoxy resin, fluorinated ethylene propylene, fluoromethacrylate, poly(arylene ether), parylene F, parylene N and amorphous polytetrafluoroethylene;

15 the casting solvent comprises at least one of deionized water, an organic monomer mixture, a water based dispersion, a water-in-oil emulsion, an oil-in-water emulsion, chlorobenzene, anisole, cyclohexanone, acetone, methyl ethyl ketone, methyl isobutyl ketone, mesityl oxide, methyl amyl ketone, cyclohexanone, methyl acetate, ethyl acetate, iso-amyl acetate, alkyl carboxylic esters, methyl t-butyl ether, dibutyl ether, methyl phenyl ether, ethoxy ethanol, butoxy ethanol, ethoxy-2-propanol, propoxy ethanol, butoxy propanol, butoxy ethoxy acetate, ethyl 3-ethoxy propionate, methanol, ethanol, propanol, iso-propanol, butanol, iso-butanol, amyl alcohol, benzene, toluene, xylene, naphthalene, mineral spirits, and 2-nitropropane; and the supercritical fluid comprises at least one of CO₂ and N₂O.

20



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/18226

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/316 H01L21/768

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 804 508 A (CHO CHIH-CHEN ET AL) 8 September 1998 (1998-09-08) the whole document	1-8 9,10
Y	---	---
X	US 5 393 712 A (KAPOOR ASHOK K ET AL) 28 February 1995 (1995-02-28) the whole document	1-8
Y	---	---
	US 5 185 296 A (MORITA KIYOKUKI ET AL) 9 February 1993 (1993-02-09) column 4, line 57 -column 5, line 9 --- -/-	9,10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

G document member of the same patent family

Date of the actual completion of the international search

18 December 2001

Date of mailing of the international search report

28/12/2001

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Pusch, C

INTERNATIONAL SEARCH REPORT

Intel Application No
PCT/US 01/18226

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PHALIPPOU J ET AL: "GLASSES FROM AEROGELS. \PART 1 THE SYNTHESIS OF MONOLITHIC SILICA AEROGELS" JOURNAL OF MATERIALS SCIENCE, CHAPMAN AND HALL LTD. LONDON, GB, vol. 25, no. 7, 1 July 1990 (1990-07-01), pages 3111-3117, XP000150744 ISSN: 0022-2461 the whole document</p>	1-8
A	<p>EP 0 453 107 A (UNIV COLORADO FOUNDATION) 23 October 1991 (1991-10-23) page 4; table 1</p>	3
A	<p>US 5 252 620 A (ELLIOTT JR JARRELL R ET AL) 12 October 1993 (1993-10-12) the whole document</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/18226

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5804508	A	08-09-1998	US 5470802 A EP 0684642 A1 JP 8162450 A US 5789819 A	28-11-1995 29-11-1995 21-06-1996 04-08-1998
US 5393712	A	28-02-1995	NONE	
US 5185296	A	09-02-1993	JP 2035458 A JP 2113525 A US 5304515 A	06-02-1990 25-04-1990 19-04-1994
EP 0453107	A	23-10-1991	US 4970093 A AT 119215 T DE 69107656 D1 DE 69107656 T2 EP 0453107 A1 JP 4228574 A	13-11-1990 15-03-1995 06-04-1995 05-10-1995 23-10-1991 18-08-1992
US 5252620	A	12-10-1993	US 5128382 A WO 9310173 A1	07-07-1992 27-05-1993